A Statistic that Identifies Errant Standard Preparation and Instrument Non-linearity Demonstrated with Mercury Standards Prepared by Blending NIST Fossil Fuel CRMs of Similar Matrices

Supporting Information

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1. Interval-repeatability: I_a and I_m Components of Uncertainty: Recognizing that I_r is the observed Interval-repeatability for two measurements taken at different concentrations that have been corrected for the difference in their mean concentrations by I_a, the increase in the uncertainty of I_r due to the uncertainty of I_a and I_m needs to be considered.

The contribution of I_m (i.e., $X_1 - X_2$) is included by definition in r and is represented in variance terms in Equation S.1 The variance associated with r includes the variances associated with its corresponding measurement method and range of matrices (i.e., material inhomogeneity).

$$\text{Var}\,(r_{(i,ii)}) = \left(\frac{\sqrt{\frac{r_i^2 + r_{ii}^2}{2}}}{1.96\sqrt{2}} \right)^2 . \qquad \text{S.1}$$

The contribution of I_a for a given interval is equal to the sum of the variances derived from the uncertainty of each standard's assigned value. This is represented in Equation S.2.

$$\text{Var}\,(I_{a(i,ii)}) = \left(\frac{U_i}{k_i} \right)^2 + \left(\frac{U_{ii}}{k_{ii}} \right)^2 . \qquad \text{S.2}$$

The total expanded uncertainty (U) of certified values includes all components of uncertainty, including material inhomogeneity. Consequently the combining of the variances given in Equations S.1 and S.2 would result in the double-counting of the variance associated with material inhomogeneity. Only the non-material components of uncertainty in the parent CRMs certified values need to be considered. Recognizing that the relative consistency of certified values is already addressed in Condition (1), if the material component of uncertainty in the certified value dominates the total uncertainty, or the measurement component of the certified value is small compared to $r_{(i,ii)}$, then the variance associated with I_a will be insignificant

compared to the uncertainty of I_r and can be ignored. If the I_a component of variance is significant, and ignored, then the I_r QC Test will impose a more conservative specification for the prepared standards to pass.

2. Interval-repeatability: Homoscedastic Case

To prove the validity of $|I_r| \le r$ with 95% probability in the homoscedastic case, denote by a_i, a_{ii} the two assigned values to be compared and m_i, m_{ii} the two corresponding measured values. The homoscedastic Interval-repeatability formulation assumes that:

$$m_i \sim N(a_i, \sigma^2),$$
$$m_{ii} \sim N(a_{ii}, \sigma^2).$$

That is, each measurand distributes Normally with assigned mean and constant variance σ^2. The sample standard deviation s_r estimates the theoretical standard deviation σ. The two measurements are assumed to be independent. Their difference according to the standard arithmetic properties of the Gaussian distribution is expressed as:

$$m_i - m_{ii} \sim N(a_i - a_{ii}, 2\sigma^2).$$

Therefore:

$$P(|I_r| \le r) = P(|(m_i - m_{ii}) - (a_i - a_{ii})| \le r),$$
$$= P(|Z|\sqrt{2\sigma^2} \le r),$$
$$= P(|Z|\sqrt{2\sigma^2} \le 1.96\sqrt{2\sigma^2}),$$
$$= P(|Z| \le 1.96),$$
$$= 0.95.$$

$Z \equiv N(0,1)$, the standard Gaussian, appears on the second line because the true mean difference $a_i - a_{ii}$ has been subtracted from the observed mean estimate difference $m_i - m_{ii}$ with resulting variance $2\sigma^2$ (standard deviation $\sqrt{2\sigma^2}$). The third line makes use of the ASTM definition of *r*, $r = 1.96\sqrt{2}\ \sigma$.

3. Interval-repeatability: Heteroscedastic Case

To prove the validity of $|I_r| \le 1.96\sqrt{\sigma_i^2 + \sigma_{ii}^2}$ with 95% probability in the heteroscedastic case (Equation 7), denote by a_i, a_{ii} the two assigned values to be compared and m_i, m_{ii} the two corresponding measured values. The heteroscedastic Interval-repeatability formulation assumes that:

$$m_i \sim N(a_i, \sigma_i^2),$$
$$m_{ii} \sim N(a_{ii}, \sigma_{ii}^2).$$

That is, each measurand distributes Normally with the mean assigned value and its own variance. The two measurements are assumed to be independent. Their difference according to the standard arithmetic properties of the Gaussian distribution is expressed as:

$$m_i - m_{ii} \sim N(a_i - a_{ii}, \sigma_i^2 + \sigma_{ii}^2).$$

Therefore:

$$P(|I_r| \le 1.96\sqrt{\sigma_i^2 + \sigma_{ii}^2}) = P(|(m_i - m_{ii}) - (a_i - a_{ii})| \le 1.96\sqrt{\sigma_i^2 + \sigma_{ii}^2}),$$
$$= P(|Z|\sqrt{\sigma_i^2 + \sigma_{ii}^2} \le 1.96\sqrt{\sigma_i^2 + \sigma_{ii}^2}),$$
$$= P(|Z| \le 1.96),$$
$$= 0.95.$$

$Z \equiv N(0,1)$, the standard Gaussian, appears on the second line because the true mean difference $a_i - a_{ii}$ has been subtracted from the observed mean estimate difference $m_i - m_{ii}$ with resulting variance $\sigma_i^2 + \sigma_{ii}^2$.

In terms of the individual repeatabilities:

$$r_i = 1.96\sqrt{2\sigma_i^2} \text{ and } r_{ii} = 1.96\sqrt{2\sigma_{ii}^2},$$

$$1.96\sqrt{\sigma_i^2 + \sigma_{ii}^2} = \sqrt{\frac{r_i^2}{2} + \frac{r_{ii}^2}{2}} = \sqrt{\frac{r_i^2 + r_{ii}^2}{2}}.$$

4. Guide for Preparation of Liquid CRM Blends

1. Use clean and dry syringes with caps, disposable pipettes, and bottles with caps, or septa, when transferring CRM material. If septa are used, than syringes require needles. **Caution:** Only a clean and dry syringe or pipette may contact the CRM material and then only to draw material out. Excess material is never returned to the stock CRM container. For syringes with caps (not needles), create an air space between the tip and the sample drawn into the syringe, so that the syringe can be capped and uncapped without loss of material.
2. For materials that are not free flowing at room temperature (e.g., some residual fuel oils and crude oils) gently heat the closed source container in a water bath until free flowing, or 65 °C (150 °F), which ever occurs first. Do **NOT** heat quickly or container may burst violently. If the heated material does not become free flowing, then it should not be used.
3. Use one balance for all weighings (≥ 0.2500 g ± 0.0005 g, or ≥ 0.02500 g ± 0.00005 g).
4. Obtain mass of components by difference, that is, weighing syringe and collection bottle with septa, or cap, before and after transfer of components. Weigh the component of lesser mass first.
5. If needed, recalculate an updated target mass for the larger component based on the actual mass of the lesser component to better hit the desired target value of the blend.

6. After transferring CRM components via syringe into a bottle, the bottle should have sufficient empty volume to facilitate mixing. Thoroughly mix the components in the bottle by holding the top and bottom of the bottle in opposite hands, and rolling each hand over the other (do not use stirrer). Care must be exercised not to introduce entrapped air.
7. Measure each blend and parent material. Combining multiple measurements (n) into a single result provides a practical means of increasing the sample mass of each replicate and in improving the efficacy of the I_r QC Test.
8. Proceed to the I_r QC Test for Blends.

5. Guide for Preparation of Solid (powdered) CRM Blends- Aliquots ONLY

1. Use one balance for all weighings (≥ 0.2500 g ± 0.0005 g, or ≥ 0.02500 g ± 0.00005 g).
2. Mix each CRM bottle by holding the top and bottom of the bottle in opposite hands, and rolling each hand over the other.
3. CRMs in powder form are to be equilibrated to the laboratory's atmosphere before weighing. Constant mass can be verified on a separate balance with a sensitivity of at least ± 0.001. The test portions and their corresponding moisture samples are to be weighed contemporaneously.
4. Weigh a sample for determination of residual moisture in order to correct the certified value of each component from a dry basis to an "as run" (i.e., as weighed basis).
5. Record the mass of the sample combustion crucible, boat or digestion bomb (alternatively tare the balance and zero the mass of the crucible). Note: To minimize potential weighing errors with a five place balance, **DO NOT** handle the crucible once it has been placed on the balance, until all components have been weighed.
6. Add the CRM component of lesser mass directly into the sample boat. To minimize deviation from the target mass, the CRM material can be placed on an auxiliary balance and tared, so that the mass of the material captured on the spatula can be seen as a negative number on this auxiliary balance and, before transfer, its mass adjusted until very near the target mass.

7. Record the combined mass of the crucible plus first component. Then calculate the mass of the lesser component by difference. Now, if desired, recalculate an updated target mass of the greater component based on the actual mass of the lesser component to better hit the desired target value of the blend. After recording the combined mass of the crucible plus first CRM component, add the second CRM component on top of first component in the crucible (Alternatively, re-tare and zero the mass of the crucible plus first CRM component). Record total mass and calculate the mass of the second component by difference.
8. Lightly tap the sample crucible to level the CRM materials in the container. **DO NOT** stir or otherwise touch the actual sample.
9. Now combust or digest the sample and measure each blend and parent CRM for the analyte of interest.
10. Proceed to the I_r QC Test for Blends.

6. I_r QC Test for Blends Requiring a Non-parent CRM *D*

1. First identify and record the repeatability limit for the analytical method (i.e., acceptable range between replicates) at each concentration measured.
2. Based on the method's scope, note the working range of the analytical method.
3. If both parents are out of the working range of the instrument, start at CRM *D* and organize samples up and down in terms of concentration from CRM *D*. For example, when the concentration of *D* is between C_2 and C_3, then *D,* $C_3 \ldots C_{j-1,}$ C_j to *B* and *D,* $C_2,$ $C_{1,}$ to *A*.
4. Using the actual mass (g) of each component CRM (i.e., *A* and *B*), calculate each blend's assigned value.
5. Determine the *Assigned Value Interval* between the CRM *D* and each successive standard by difference. Include all blends (i.e., C_1 to C_j), parent CRMs *A* and *B*.

6. In the same manner as described in step 5, determine the corresponding *Measured Value Intervals,* that is, the intervals between the CRM *D* and each successive measured value.
7. **Successful** blending is indicated whenever the absolute value of the observed Interval-repeatability, I_r, (difference between corresponding Measured Value Interval *(i,ii)* and Assigned Value Interval *(i,ii)*) is less than or equal to the method's predicted Interval-repeatability limit, $r_{(i,ii)}$ (see Equation 8).
8. Unsuccessful blends are to be removed from the sequence of blends and an updated I_r QC Test is performed. Intervals involving parent end members are to be included in the data used in the test, but only intervals between CRM *D* and the blends in the range of subsequent use are required to pass (because, depending on the ratio of the blend and the linearity of the instrument, one or both of the parents, and some of the possible blends, may be out of the linear concentration range of interest). A minimum of two standards in the range of interest, e.g., one CRM (*A, B,* or *D)*, and one blend, are needed to perform an I_r QC Test. Note: the investigation of I_r with other blend combinations than those mentioned in the QC test above can provide additional valuable information.
9. Save a summary of I_r QC Test with other details of your blending process for your records.

7. Fossil Fuel SRMs Successfully Tested for Blending Within Their Matrix for Sulfur and Mercury:

Middle Distillates

1616b Sulfur in Kerosene

1617a Sulfur in Kerosene

1624d Sulfur in Diesel Fuel Oil

2723a Sulfur in Diesel Fuel Oil

2724b Sulfur in Diesel Fuel Oil

2770 Sulfur in Diesel Fuel Oil

2771 Sulfur in Diesel Fuel Blend Stock

Petroleum Coke

2718 Trace Elements in Green Petroleum Coke

2719 Trace Elements in Calcined Petroleum Coke

Bituminous Coal

1632d Trace Elements in Bituminous Coal

2683b Bituminous Coal

2684b Bituminous Coal

2685b Bituminous Coal

2692b Bituminous Coal

2692c Bituminous Coal

2693 Bituminous Coal

Metallurgical Coke

2775 Foundry Coke

2776 Furnace Coke